MeV ION DAMAGE IN III-V SEMICONDUCTORS: SATURATION AND THERMAL ANNEALING OF STRAIN IN GaAs AND GaP CRYSTALS*

C. R. WIE**, T. VREELAND, JR., and T. A. TOMBRELLO
Divisions of Physics, Mathematics, and Astronomy, 301-38 and
Engineering and Applied Science,
California Institute of Technology, Pasadena, California 91125

ABSTRACT

MeV ion irradiation of GaAs crystals at room temperaure has shown that the lattice strain perpendicular to the sample surface saturates to $\sim 0.4\%$ for <100> cut and $\sim 0.3\%$ for <111> and <110> cut crystals with zero parallel strain in all cases. In this paper, the thermal recovery behavior of the saturated strain in GaAs (100) is presented for a 15 min isochronal annealing. The recovery of strain depth profile is shown explicitly by a dynamical theory analysis of the x-ray rocking curves taken after each annealing step. The isochronal recovery behavior of strain suggests that a spectrum of activation energies is involved in the thermal migration of defects in the saturated surface layer. This also suggests that many kinds of antisite defect complexes exist in the surface layer. The strain and related defects are also shown to saturate in MeV ion bombarded GaP (100) crystals. This may indicate that all the primary defects (interstitials, vacancies, and antisite defects) saturate under MeV ion irradiation of III-V compounds, and support the proposed ion-lattice single collision model of defect production and saturation under MeV ion irradiation. The linewidths of x-ray rocking curves obtained from GaP crystals bombarded at room temperaure and at ~ 490 K indicate that low-temperature recovery stage defects cause major crystal distortion in III-V compounds. Also presented are the isochronal annealing behaviors of lattice strain, x-ray broadening, and peak reflecting power of room temperature irradiated GaP (100) crystals.

Submitted to Nuclear Instruments and Methods in Physics Research B

---

*Supported in part by the National Science Foundation [DMR83-18274] and the Caltech President's Fund.
**Permanent address: Dept. of Electrical & Computer Eng., SUNY at Buffalo, Amherst, NY 14260.

ONE OF THE BROWN BAG PREPRINT SERIES
IN BASIC AND APPLIED SCIENCE

September 1985

I. Introduction

X-ray rocking curve measurements of lattice strain have been proved to be an efficient and nondestructive technique in the study of radiation damage in single crystals [1]. This technique has been applied to the studies of MeV ion damage in CaF_2 and GaAs single crystals [2,3], and to ion implantation in Si, Ge, and GaAs single crystals [4]. This technique is also capable of measuring the thickness and lattice parameter mismatch in strained layer superlattices (SLS) [5]. To extract information on strain and damage profiles from the rocking curves, a kinematical or a dynamical x-ray diffraction theory is used for the analysis [1,6,7,8].

Various techniques are used in the study of radiation damage in semiconductors. The techniques and their sensitive ranges in defect concentration are as follows [9]: electrical resistivity or photoconductivity for 10^{-9}-10^{-5}, EPR for 10^{-9}-10^{-3}, optical absorption for 10^{-8}-10^{-3}, and anelastic, lattice dilatation and stored energy measurements for 10^{-5}-10^{-3} atomic fraction defect concentrations. In practice MeV electron irradiation can produce defects up to 10^{-6} atomic fraction, and MeV ions produce defects of 10^{-6}-10^{-2} atomic fraction by an irradiation of less than an hour.

We have reported that the perpendicular strain in MeV ion irradiated GaAs (100) crystals saturates at $\sim 0.4\%$ regardless of the sample electronic property [3]. In a recent paper [10], we reported that the perpendicular strain in <111> and <110> cuts of GaAs crystals saturates at $\sim 0.3\%$ with negligibly small parallel strain in all cases, and showed that the strain is produced by nuclear collisions, and partially annealed by simultaneous electronic ionization processes [10]. An ion-lattice single collision model, which can be applied to the radiation damage by MeV ions or MeV electrons, explains the saturation of point defects and predicts the dependence of point defect concentrations on the beam dose in the low dose limit, the nuclear stopping power, and the electronic stopping power [10]. We suggest that the strain produced in 300 K irradiated GaAs crystals is controlled by antisite defects and their complexes.

In this paper, we report the study of MeV ion damage in Zn-doped p-type GaP (100) crystals, and the thermal annealing study of perpendicular strain in GaAs and of strain, x-ray broadening and peak reflecting power in GaP.

II. Experimental Results and Discussion

A 15 MeV Cl ion beam was incident on Cr-doped p-type semi-insulating (100), (110), and (111) cut GaAs crystals, and Zn-doped p-type (100) cut GaP crystals. The irradiation was made at 300 K for GaAs and GaP crystals, and also at $\sim$ 490 K for a GaP crystal. The x-ray rocking curves were taken from the bombarded samples. Isochronal ($\sim$ 15 min) or isothermal annealing was performed on GaAs (100) and GaP (100) crystals bombarded at 300 K, and the x-ray rocking curves were measured after each annealing step.

Fig. 1 shows the x-ray rocking curves for a symmetric (400) reflection from 15 MeV Cl ion bombarded GaAs (100) crystals at 300 K. The rocking curve pattern developing at negative angles for increasing beam dose corresponds to the strain profile in the surface layer whose thickness is equal to the ion range, and the peak at zero angle is the reflection from the undamaged substrate cyrstal beyond the ion range. Development of a single peak at around -0.22 degrees indicates the saturation of perpendicular strain at $\sim$ 0.4% in GaAs (100). For <111> and <110> cut crystals, the perpendicular strain saturates at $\sim$ 0.3%. The linewidths of the strain peak are relatively small ($\sim$ 0.02 degrees) after saturation. The symmetric shape and small x-ray broadening implies a uniform lattice spacing with small lattice distortion.

Rocking curves for a GaP (100) crystal bombarded at 300 K are given in Fig. 2. The initial development of the rocking curve profiles is similar to that of GaAs except for the one for a high dose (2.4×10^{15} cm^{-2}). The strain peak of the high dose curve is symmetric with large linewidth compared to the corresponding peak for GaAs, which implies strain saturation with high lattice distortion in 300 K bombarded GaP crystals.

Fig. 3 shows the isochronal recovery stages of point defects in III-V semiconductors, taken from the paper by Lang et al. [11]. We should note that some defects are mobile at 300 K in GaAs; however, all the defects are stable at 300 K in GaP. Thus, it seems reasonable to postulate that low-temperature recovery stage defects cause major crystal distortion in III-V semiconductors. Hence, we irradiated a GaP crystal at $\sim$ 490 K so that some defects would be mobile during the irradiation. Fig. 4 shows the rocking curves taken from this sample. The width (FWHM) of the strain peak is comparable to that of GaAs; thus, our postulate seems to be verified. In reference 10, we suggested that the defects producing the strain in 300 K irradiated GaAs are mainly antisite defects and their complexes. The same thing may be true in the GaP crystal bombarded at 490 K.

The high dose (2.4×10^{15} cm^{-2}) bombarded GaAs (100) and GaP (100) crystals, irradiated at 300 K, were annealed for 15 mins at each temperature under the forming gas (15% H_2, 85% N_2) flow. The samples were cooled to room temperature and the rocking curves were taken. The perpendicular stain was obtained from the angular separation between the strain peak and the substrate peak.

The recovery behavior of strain depth profiles in Cr-doped semi-insulating GaAs (100) crystals bombarded to 1.2×10^{15} cm^{-2} at 300 K is shown in Fig. 5. The depth profiles after each step of annealing were obtained by a dynamical theory analysis of the rocking curves [8]. Details of the theory and the analysis technique are given in a separate paper [8]. The figure explicitly illustrates the depth distribution after each anneal step, and shows that the strain is completely annealed at 500°C, except for the region of maximum nuclear stopping power. The strain in the region around the end of the ion range was found to completely recover after a 700°C annealing.

Fig. 6 presents the fraction of strain recovered in GaAs (100) crystals as a function of annealing temperature. Generally, a gradual recovery is observed over the temperature range from 300 K to 700 K with small distinct stages at around 500 K and 670 K. One sample bombarded with the same ion to the same dose as the samples used in Fig. 6 was used for an isothermal annealing of 8 min time steps.

The isothermal annealing data in Fig. 7 suggests that annealing has occured for all the strain associated with activation energies below that reached at the end of each annealing step at a given temperature. The characteristic activation energy, E_a, at the end of each step of annealing is defined by $K_B T \ln(\nu t)$, where ν is the frequency factor (approximately given by $k_B T/_h$), t is the annealing time, k_B the Boltzmann constant, T the temperature, and h the Planck constant. The strain change which has occured in each step of annealing, $\Delta\varepsilon$, is approximately the integral of the activation energy spectrum from E_{a1} (the value of E_a at the end of previous annealing) to E_{a2} (the value of E_a at the end of the present annealing step). Then, $\frac{\Delta\varepsilon}{(E_{a2} - E_{a1})}$ is the average value of the activation energy spectrum of strain between E_{a1} and E_{a2}, and plotting it against E_a gives an approximate block graph of the activation energy spectrum. The isochronal anneal data in Fig. 6 were analyzed in this way, and the result is given in Fig. 8. The same approach has been used by Primak et al. to analyze the annealing data of radiation induced lattice dialation of diamond and silicon carbide [12].

In a previous paper [10], we suggested that the strain in 300 K irradiated GaAs crystals was probably controlled by antisite defects and their complexes. This conclusion was based on the stopping power dependence of the strain and the point defects analyzed by an ion-lattice single collision model. The isochronal and isothermal annealing data in Figs. 6 and 7 indicate that the activation energy involved is not a single value, but instead it is composed of a spectrum of energies as shown in Fig. 8. We note, however, that a slightly higher recovery rate at $\sim$ 500 k is consistent with the vacancy recovery stage in GaAs [11], and the complete recovery of strain at 700 K $\sim$ 750 K occurs around the recovery stage of isolated antisite defects in GaAs [13].

If there were no recovery of defects after they are once produced by irradiation, the displacement collision cross section of $\sim 6 \times 10^{-17}$ cm^2 for 15 MeV Cl ions, for a beam dose of 2.4×10^{15} ions/cm^2 would result in $\sim$ 10 atomic % defect concentration. Even though there will be a substantial recovery of defects during the 300 K irradiation, the defect concentration should be still sufficiently high as to exist as defect pairs or complexes. Many different kinds of antisite defect pairs or complexes such as antisite-vacancy, antisite-antisite, or antisite-interstitial pairs may account for the more or less smooth recovery data (Fig. 6), where the complete relaxation at 700 K $\sim$ 750 K corresponds to the recovery of isolated antisite defects in GaAs.

For the Zn-doped p-type GaP (100) bombarded at 300 K, the isochronal anneal data are given in Fig. 9 for the perpendicular strain, x-ray broadening and peak reflecting power of the strain peak. The annealing was done over the temperature range of 300 K - 490 K. After 73 days of aging at 300 K, the strain and x-ray broadening have recovered by 13% and 32%, respectively, from their initial values in the as-bombarded sample. The 300 K recovery may be due to the slow migration or annihilation of low recovery stage defects like close Frenkel pairs. The rather high decrease in x-ray broadening by 300 K aging compared to the decrease in strain supports our suggestion that low recovery stage defects cause major lattice distortion and the strain is largely produced by antisite defects and their complexes. There is a distinct recovery stage at 360 K - 380 K in the x-ray broadening.

III. Summary

The saturation (perpendicular) strain in GaAs single crystals bombarded at 300 K with MeV heavy ions is $\sim$0.4% for <100> cut, and $\sim$0.3% for <110> and <111> cut. The parallel strain was negligibly small in all cases. The perpendicular strain in Zn-doped p-type GaP (100) crystals bombarded at 300 K saturates at $\sim$0.21%. The x-ray broadening of (saturation) strain peak is $\sim$0.02 degrees for GaAs (100), $\sim$0.09 degrees for GaP (100) bombarded at 300 K, and $\sim$0.01 degrees for GaP (100) bombarded at 490 K; this indicates that low recovery stage defects in III-V semiconductors cause major crystal distortion.

The isochronal and isothermal anneal data for GaAs (100) crystals bombarded at 300 K indicate that a spectrum of activation energies is involved in the strain recovery. In the isochronal annealing data, small recovery stages could be identified at $\sim$500 K and $\sim$660 K. The complete recovery of perpendicular strain occurs at $\gtrsim$ 700 K which agrees with the recovery stage of isolated antisite defects in GaAs. The annealing data are consistent with our suggestion that the strain in GaAs bombarded at 300 K is controlled by isolated antisite defects and their complexes (such as antisite-vacancy, antisite-antisite, or antisite-interstitial pairs).

We also presented the data on isochronal annealing of GaP (100) crystals irradiated at 300 K, for the perpendicular strain, x-ray broadening and peak reflecting power of strain peaks. After aging 73 days at 300 K the x-ray broadening decreases by $\sim$ 32% whereas the strain drops by $\sim$ 12% from the values in as-bombarded sample. This may be due to the slow recovery of close pairs. A distinct decrease in x-ray broadening of GaP strain peak occurs at 350 K – 380 K.

Acknowledgement

The authors would like to thank Dr. S. T. Picraux at Sandia National Laboratory for supplying GaP crystals and the helpful discussions at the MRS Meeting, 1984.

Figure Captions

Figure 1: FeKα1 (400) reflections from 15 MeV Cl ion bombarded GaAs (100) crystals. Ion doses are shown in the figure. Development of a single peak at -0.22 degrees indicates strain saturation. The small peak at zero angle is from the undamaged substrate crystal beyond the ion range.

Figure 2: Rocking curves for Zn-doped GaP (100) crystals bombarded with 15 MeV Cl ions at 300 K. The strain peak for 2.4×10^{15} cm^{-2} beam dose is much broader than that for a corresponding peak in GaAs.

Figure 3: Isochronal recovery stages in InSb, InAs, GaSb, GaAs, and GaP as a function of Debye temperature Θ_D. There are some defects which are mobile at 300 K in GaAs, and all defects are stable at 300 K in GaP. The line through the data shows the Θ_D^2 dependence. This figure was taken from reference 11.

Figure 4: FeKα1 (400) reflection from a GaP (100) crystal bombarded at 490 K. The strain peak is much narrower, and indicates much less lattice distortion than for the sample bombarded at 300 K.

Figure 5: The depth profiles of strain after each annealing step in 15 MeV Cl ion bombarded GaAs (100). The strain around the 5 μm region recovers after a 700^{o} C annealing. The sample was irradiated at 300 K.

Figure 6: Isochronal annealing data for GaAs (100) bombarded at 300 K with 15 MeV Cl ions to 2.4×10^{15} cm^{-2}. There are small recovery stages at 500 K and ∿ 660 K. The complete recovery of strain occurs at ∿ 725 K.

Figure 7: Isothermal anneal data obtained from GaAs (100) crystals bombarded with the same ion to the same dose as the samples in Fig. 6.

Figure 8: The activation energy spectrum of strain in 15 MeV Cl ion bombarded GaAs (100) at 300 K. This was obtained from the strain recovery data in Fig. 6. The dashed curve is a common smooth curve for both sets of data.

Figure 9: Isochronal annealing data for strain, x-ray broadening, and peak reflecting power of GaP (100) crystals bombarded at 300 K with a 15 MeV Cl ion beam to the beam dose of 2.4×10^{15} cm^{-2}.

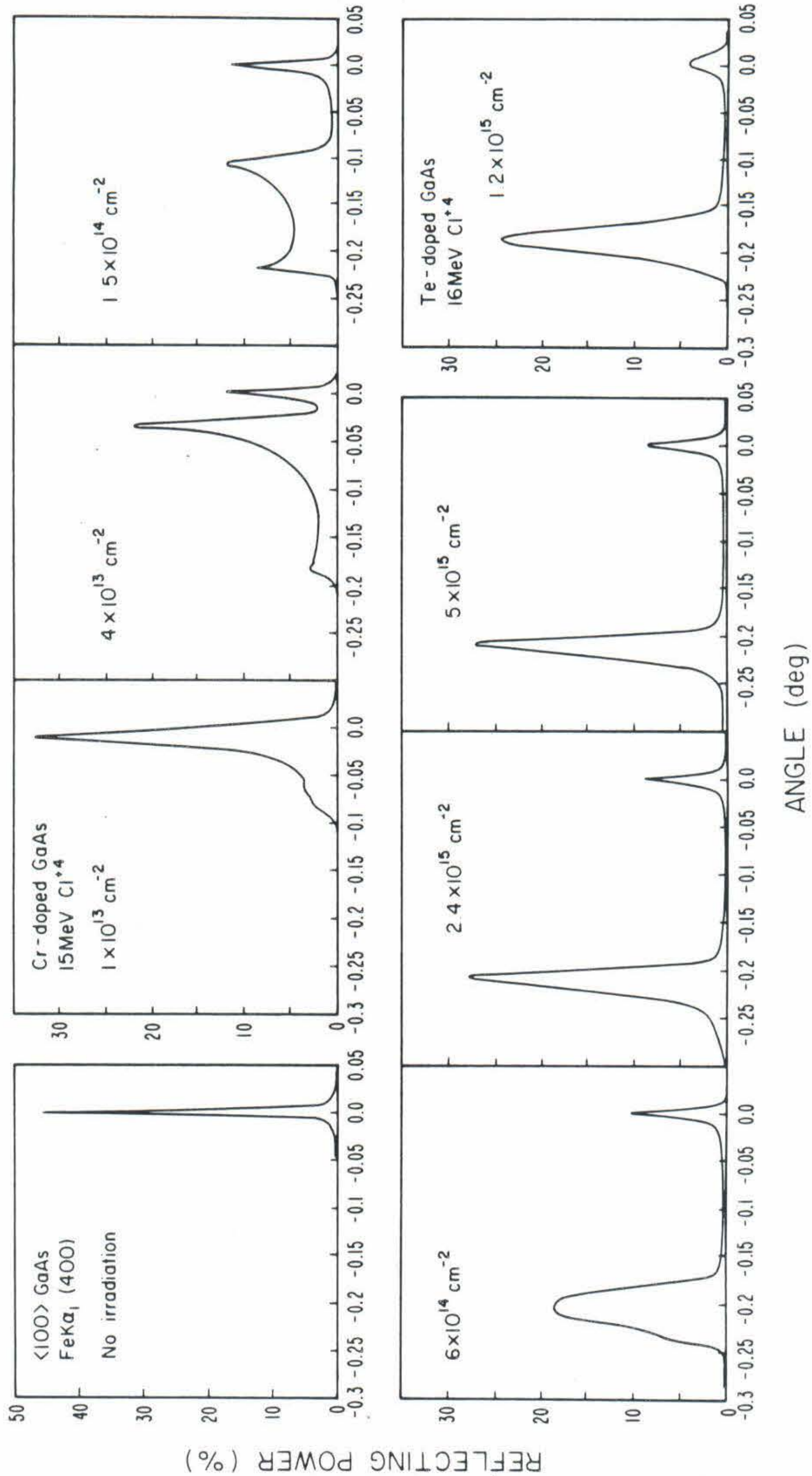

<100> GaAs
FeKa$_1$ (400)
No irradiation
Cr-doped GaAs
15MeV Cl^{+4}
1×10^{13} cm^{-2}
4×10^{13} cm^{-2}
1.5×10^{14} cm^{-2}
6×10^{14} cm^{-2}
2.4×10^{15} cm^{-2}
5×10^{15} cm^{-2}
Te-doped GaAs
16MeV Cl^{+4}
1.2×10^{15} cm^{-2}
ANGLE (deg)
REFLECTING POWER (%)

Fig. 1

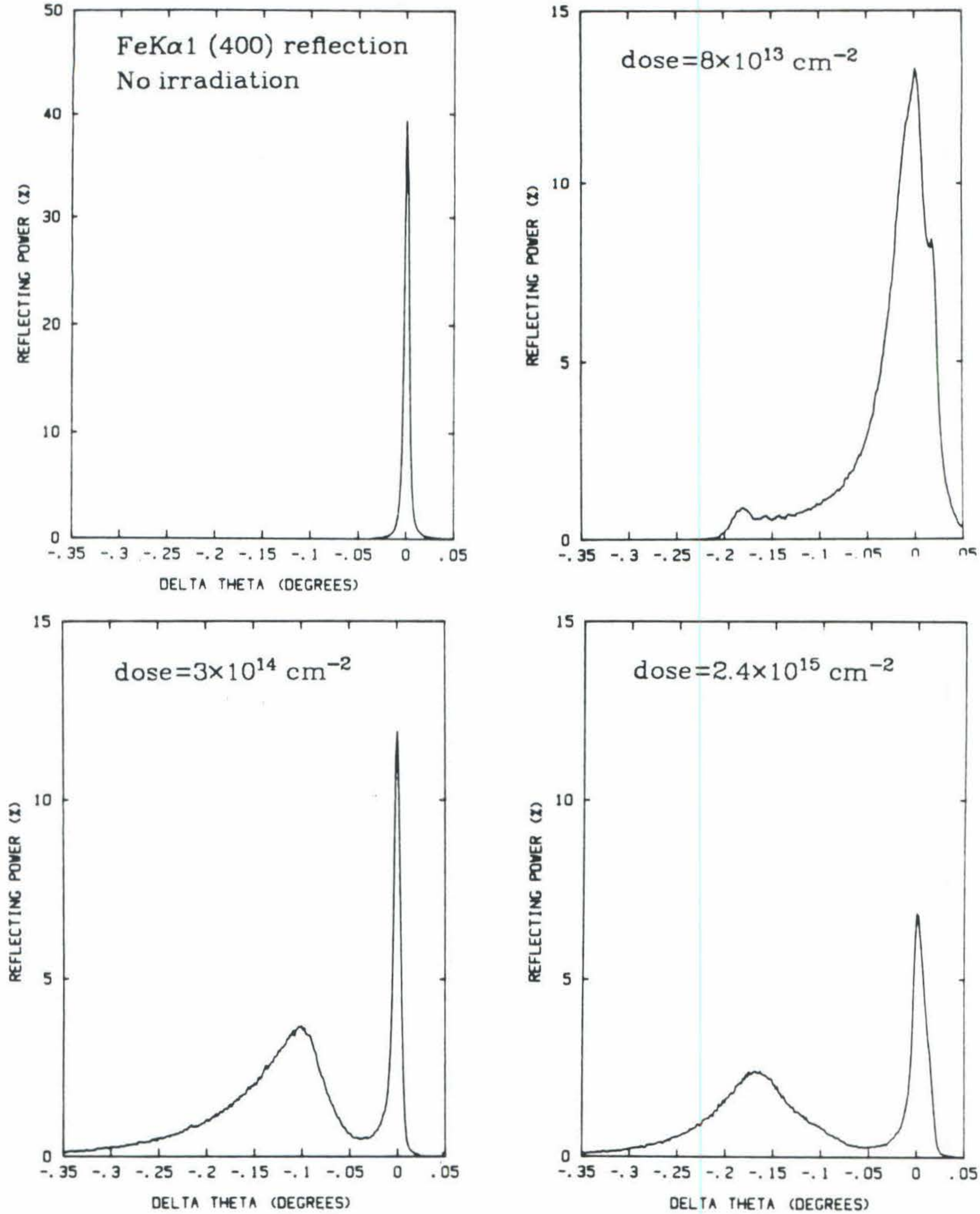

FeKα1 (400) reflection
No irradiation
dose=8×10^{13} cm^{-2}
dose=3×10^{14} cm^{-2}
dose=2.4×10^{15} cm^{-2}
REFLECTING POWER (%)
DELTA THETA (DEGREES)

Fig. 2

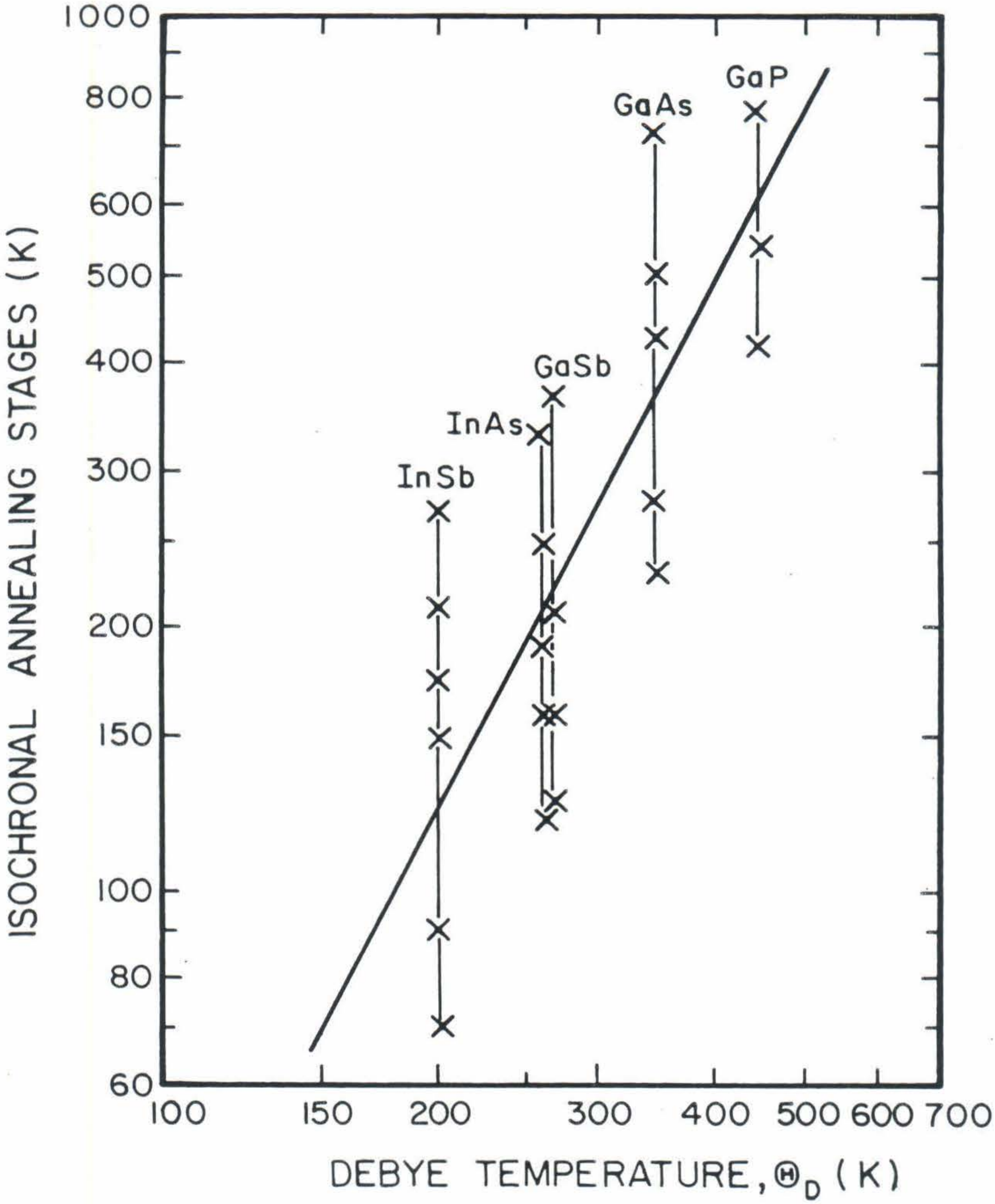

1000
800
600
500
400
300
200
150
100
80
60
100
150
200
300
400
500 600 700
ISOCHRONAL ANNEALING STAGES (K)
DEBYE TEMPERATURE, Θ_D (K)
GaP
GaAs
GaSb
InAs
InSb

Fig. 3

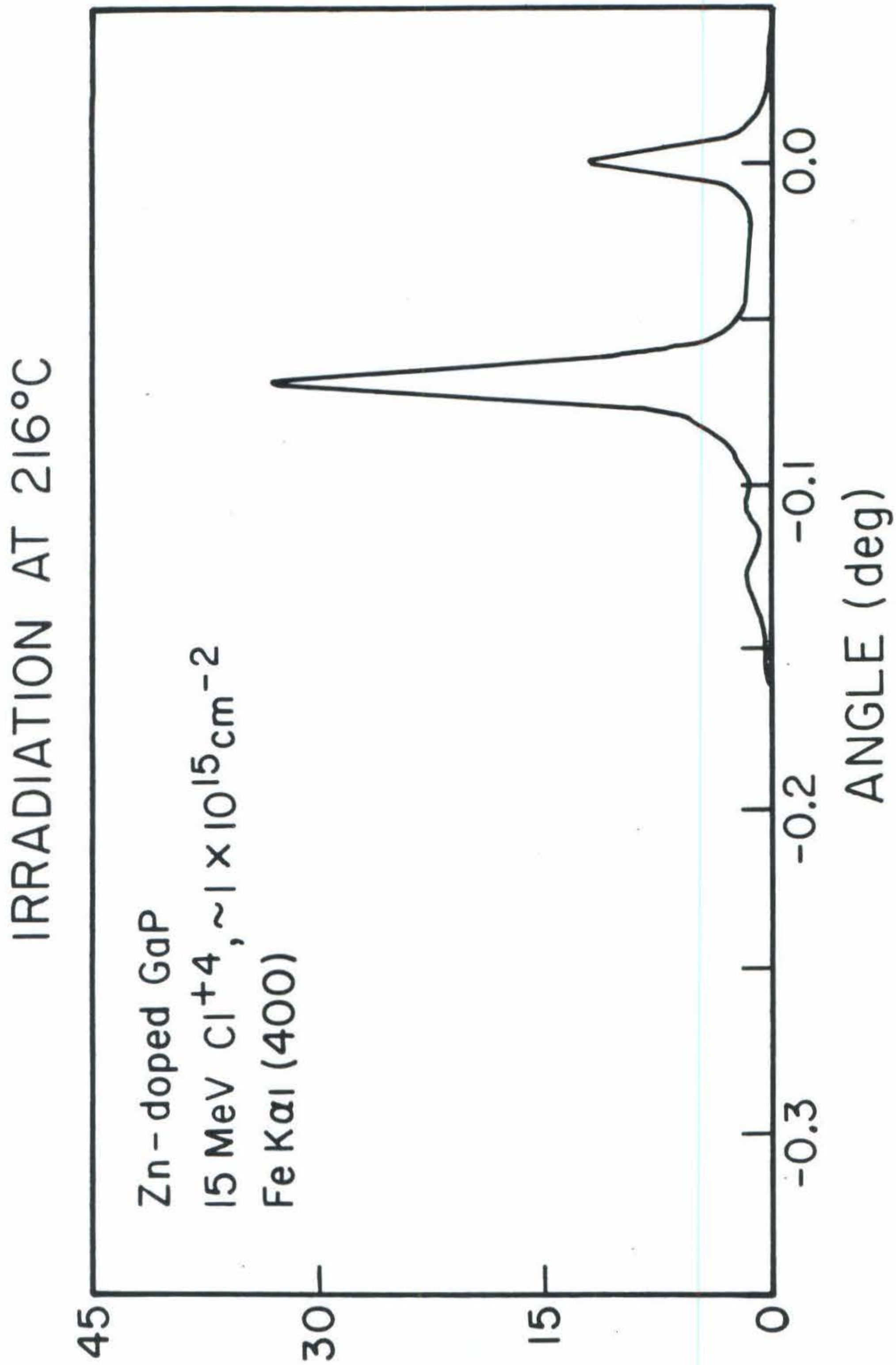
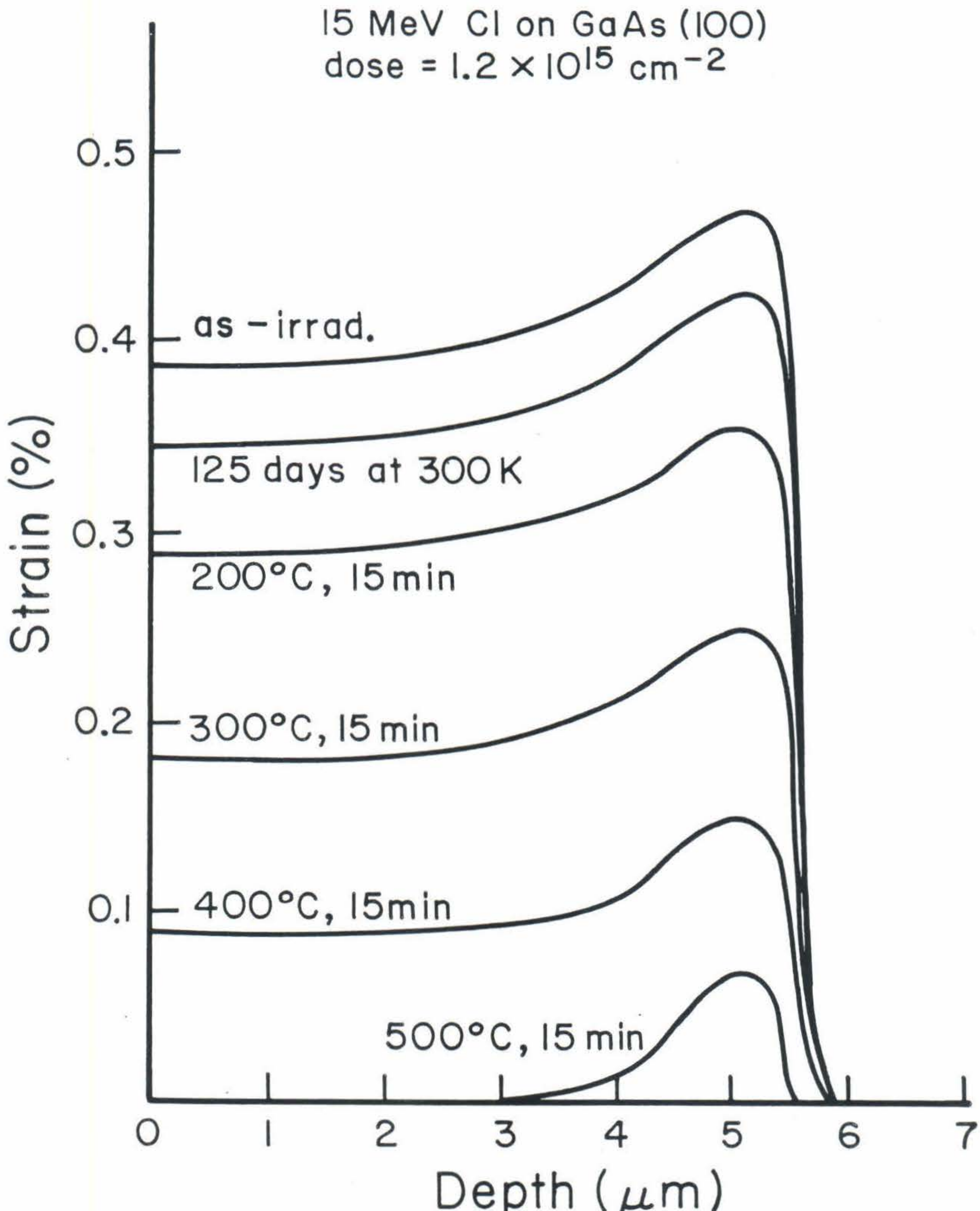
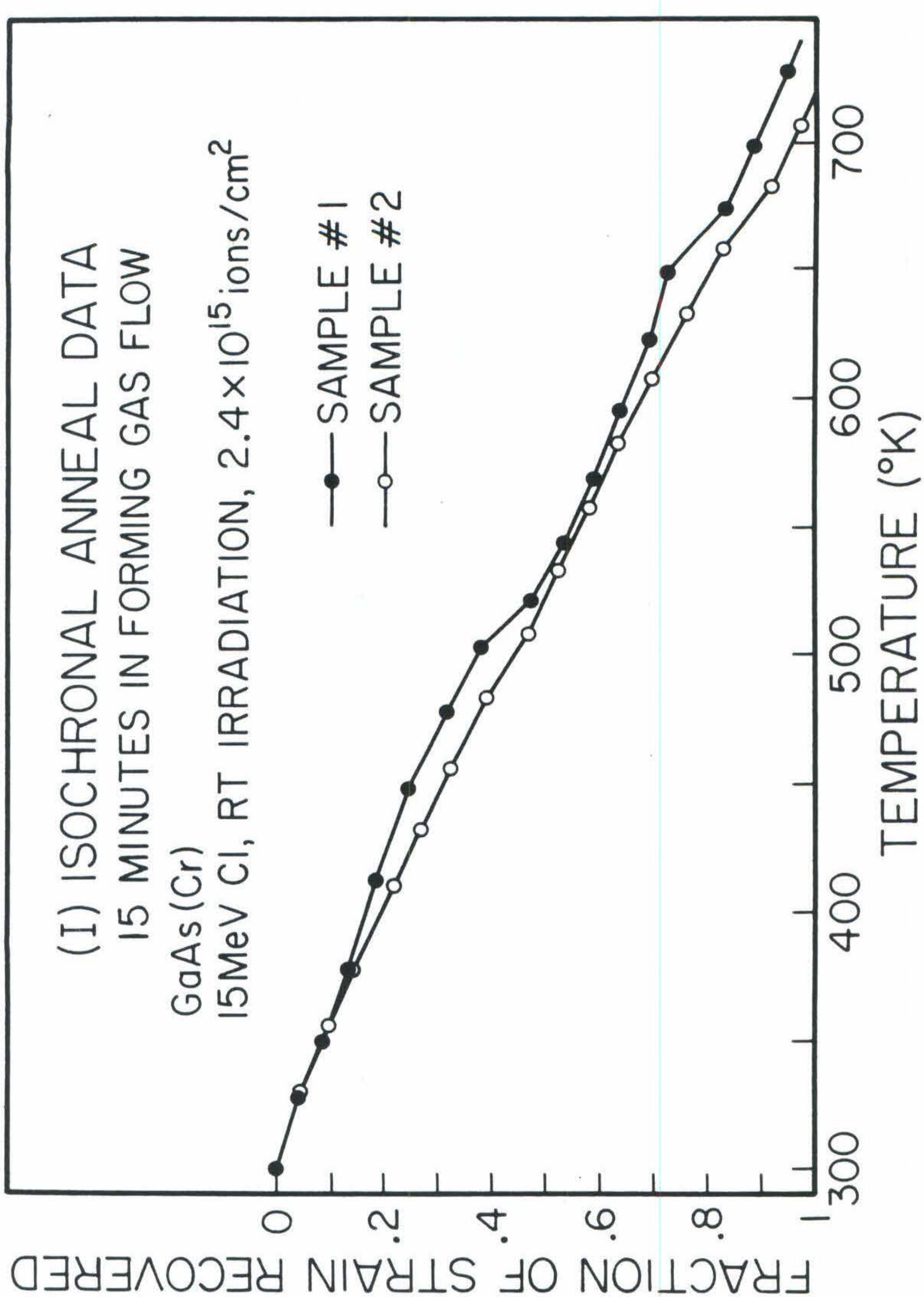

IRRADIATION AT 216°C
Zn-doped GaP
15 MeV Cl^{+4}, ~$1 \times 10^{15} cm^{-2}$
Fe $K\alpha_1$ (400)
-0.3
-0.2
-0.1
0.0
ANGLE (deg)
45
30
15
0
REFLECTING POWER (%)

Fig. 4



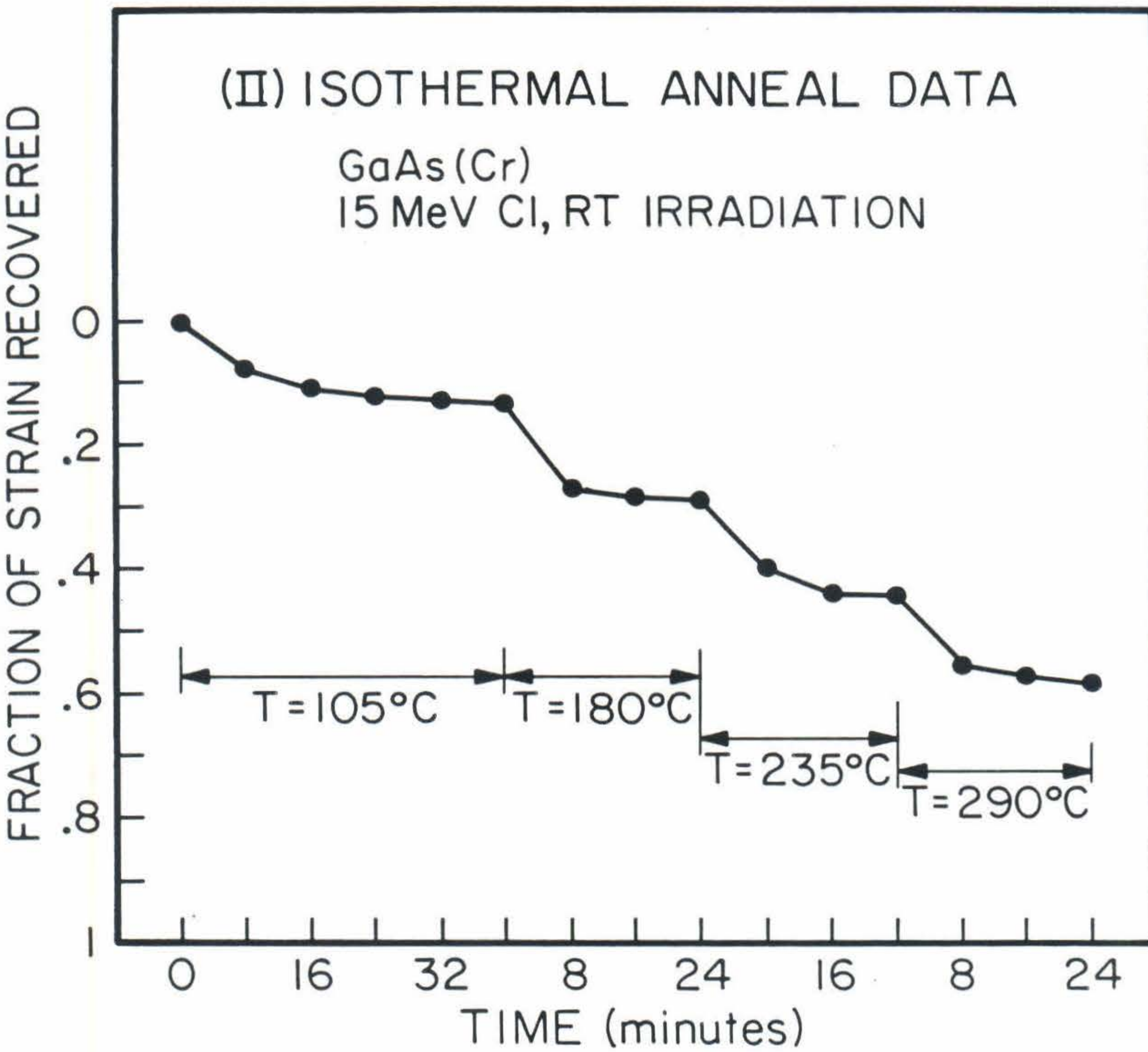
15 MeV Cl on GaAs (100)
dose = 1.2 × 10^15 cm^-2
Strain (%)
0.5
0.4
0.3
0.2
0.1
as - irrad.
125 days at 300 K
200°C, 15 min
300°C, 15 min
400°C, 15 min
500°C, 15 min
0
1
2
3
4
5
6
7
Depth (μm)

Fig. 5



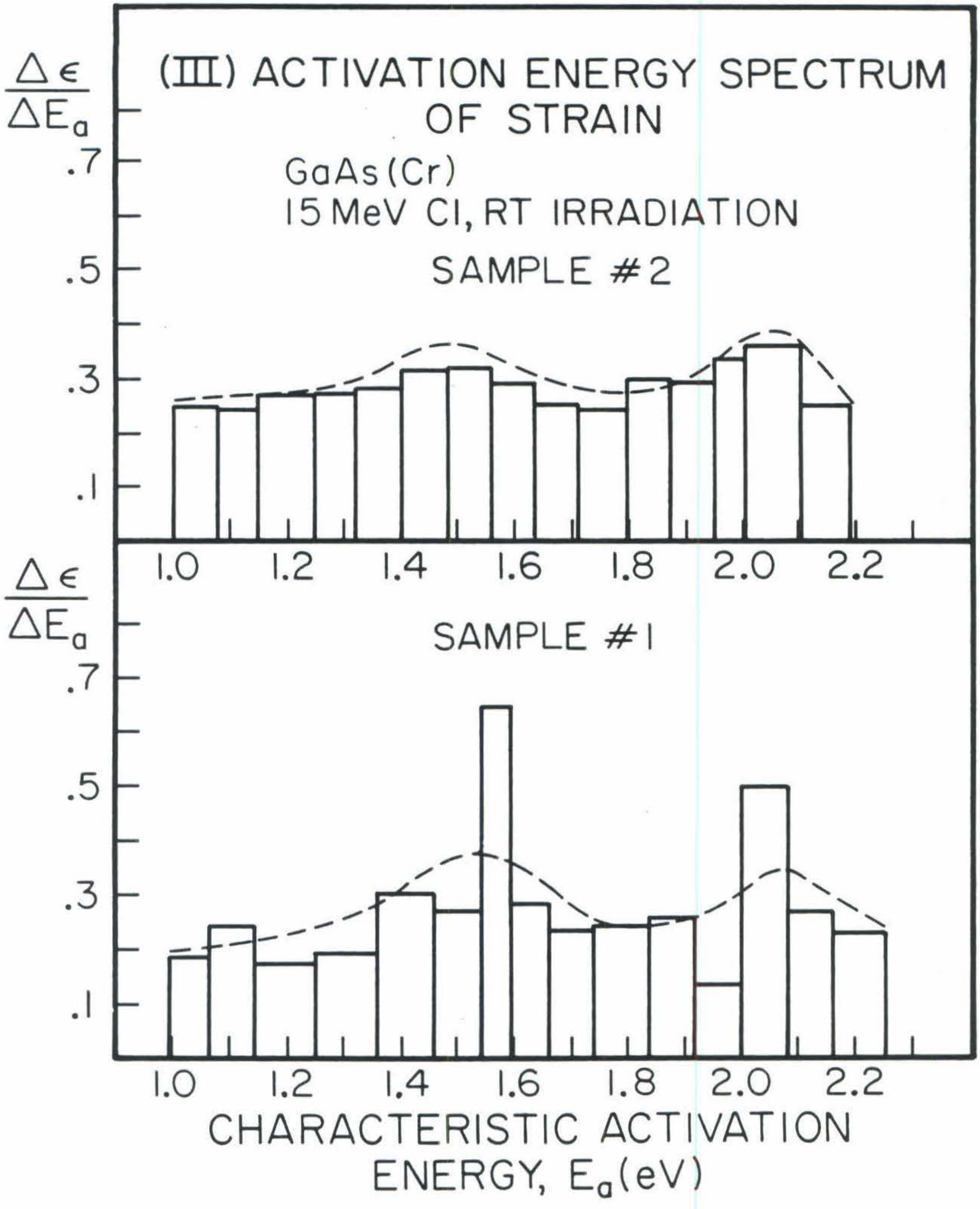
(I) ISOCHRONAL ANNEAL DATA
15 MINUTES IN FORMING GAS FLOW
GaAs (Cr)
15MeV Cl, RT IRRADIATION, 2.4×10^{15} ions/cm^2
SAMPLE #1
SAMPLE #2
300
400
500
600
700
TEMPERATURE (°K)
0
.2
.4
.6
.8
1
FRACTION OF STRAIN RECOVERED

Fig. 6



(II) ISOTHERMAL ANNEAL DATA
GaAs (Cr)
15 MeV Cl, RT IRRADIATION
FRACTION OF STRAIN RECOVERED
0
.2
.4
.6
.8
1
T = 105°C
T = 180°C
T = 235°C
T = 290°C
0
16
32
8
24
16
8
24
TIME (minutes)

Fig. 7



(III) ACTIVATION ENERGY SPECTRUM OF STRAIN
GaAs(Cr)
15 MeV Cl, RT IRRADIATION
SAMPLE #2
SAMPLE #1
$\frac{\Delta\epsilon}{\Delta E_a}$
.7
.5
.3
.1
1.0
1.2
1.4
1.6
1.8
2.0
2.2
CHARACTERISTIC ACTIVATION ENERGY, E_a(eV)

Fig. 8

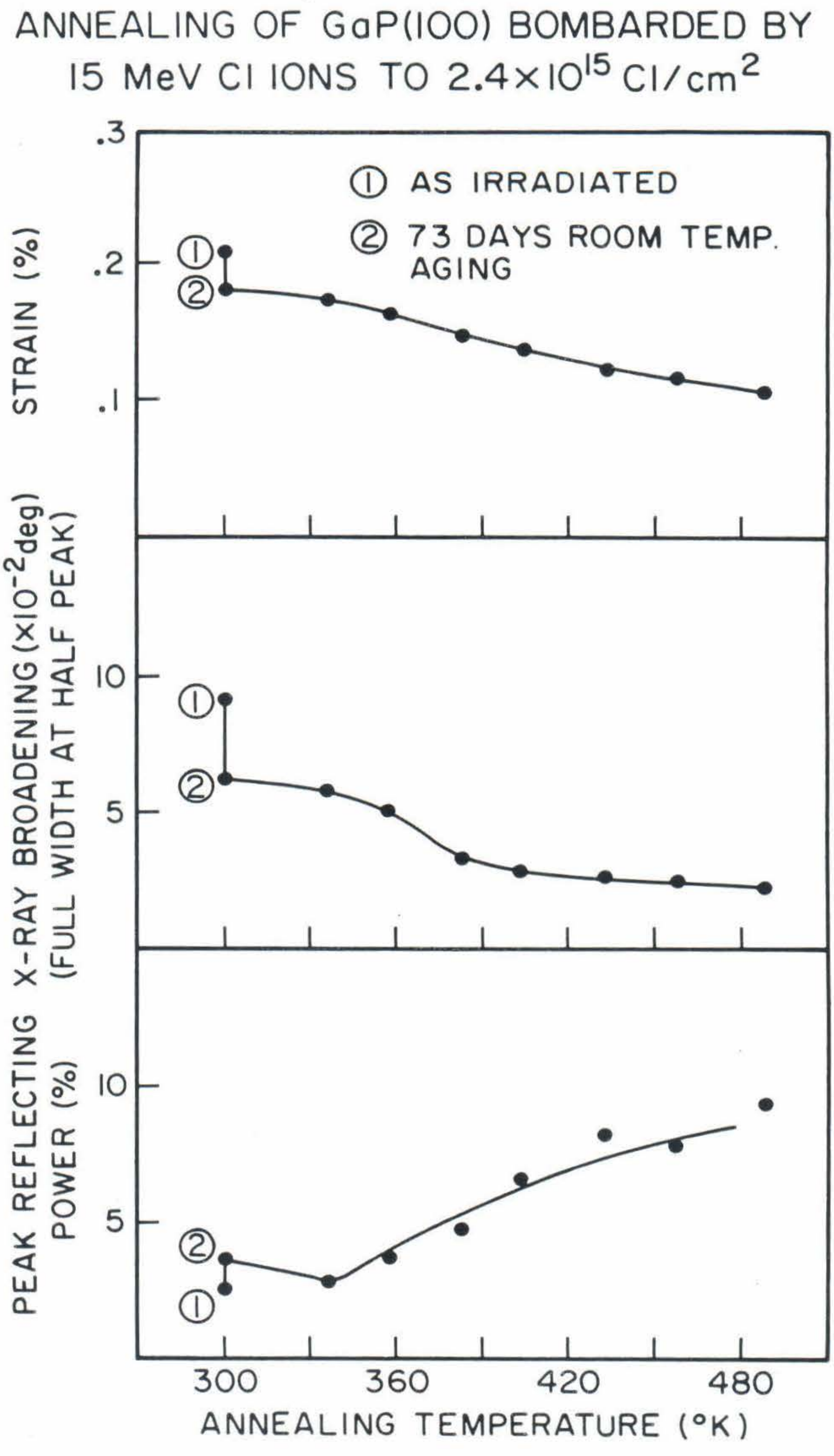

ANNEALING OF GaP(100) BOMBARDED BY
15 MeV Cl IONS TO 2.4×10^15 Cl/cm^2
① AS IRRADIATED
② 73 DAYS ROOM TEMP. AGING
STRAIN (%)
.3
.2
.1
X-RAY BROADENING (×10^-2 deg)
(FULL WIDTH AT HALF PEAK)
10
5
PEAK REFLECTING POWER (%)
10
5
300
360
420
480
ANNEALING TEMPERATURE (°K)

Fig. 9

References

[1] C. R. Wie, Ph.D. Thesis, California Institute of Technology (1985).

[2] C. R. Wie, T. Vreeland, Jr., and T. A. Tombrello, Nucl. Instr. Meth. B9, 25 (1985).

[3] C. R. Wie, T. Vreeland, Jr., and T. A. Tombrello, Mat. Res. Soc. Symp. Proc. Vol. 35, p. 305.

[4] V. S. Speriosu, B. M. Paine, M-A. Nicolet, and H. L. Glass, Appl. Phys. Lett. 40, 604 (1982).

[5] V. S. Speriosu and T. Vreeland, Jr., J. Appl. Phys. 56, 1591 (1981).

[6] B. C. Larson and J. F. Barhorst, J. Appl. Phys. 51, 3181 (1981).

[7] V. S. Speriosu, J. Appl Phys. 52, 6094 (1981).

[8] C. R. Wie, T. Vreeland, Jr., and T. A. Tombrello, submitted to J. Appl. Phys. (1985).

[9] J. W. Corbett, Solid State Physics, ed. Seitz and Turnbull, Suppl. 7 (1966) p. 45.

[10] C. R. Wie, T. A. Tombrello, and T. Vreeland Jr., submitted to Phys. Rev. B (1985).

[11] D. V. Lang, R. A. Logan, and L. C. Kimmerling, Phys. Rev. B 15, 4874 (1977).

[12] W. Primak, L. M. Fuches, and D. P. Day, Phys. Rev. 103, 1184 (1956).

[13] R. Worner, U. Kauffman, and J. Schneider, Appl. Phys. Lett. 40, 141 (1982).